

In Situ Electrochemical Quartz Crystal Microbalance Study of the Dissolution of Gold Electrodes in Hydroxamic Acid Solution containing Nitric Ion.

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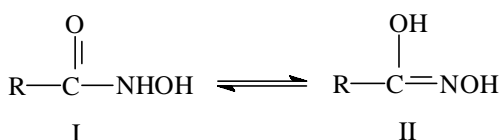
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Gold is renowned for its chemical stability. However, this stability is compromised in acid solutions under anodic conditions and in the presence of certain anions such as chloride. Due to its particular importance in both the electronics industry and the recovery of gold from mineral ores, the mechanism of the (electro-)oxidation of gold in acid media, and the products of this oxidation, have received considerable attention and a number of reviews have been published on the subject [1].

Hydroxamic acids (HAs, **Fig.1**) play a variety of important roles as metal chelating agents. Through the reactive –CONHOH group, HAs can form highly stable four or five member cyclic metal chelates of the O-O or N-O type with ferrous, non-ferrous and rare earth metals.



The strong tendency of the HAs toward complexation with most of the valuable metals/metal oxides has led to HAs being used extensively in extractive metallurgy. However, to our knowledge neither the electrochemistry of HAs on Au, or the capacity for HAs to act as hydro-metallurgical extracting agents for Au has been studied.

Under certain conditions, HAs hydrolyse into the parent acid and hydroxylamines. Indeed, complexation by certain metal ions can catalyse this process or result in the oxidative decomposition of the ligand, although the thermodynamics of this process are ill-characterised. Rational application of HAs in extractive hydrometallurgy demands quantitative knowledge of the thermodynamic stabilities of a range of HAs and their metal chelates. Thus, in order to study HA-assisted electro-oxidative dissolution of Au, and in order to better understand the role played by HA oxidation in this process, we have investigated the electro-oxidation of acetohydroxamic acid (AHA) using the electrochemical quartz crystal microbalance (EQCM) and Au microdisc electrodes.

While the EQCM provides a means of mechanism elucidation, the use of microelectrodes provides a means of obtaining thermodynamic and kinetic parameters for the system. However, thermodynamic parameters may only be obtained from microelectrode experiments conducted under near-polarographic conditions i.e. sweep rates of 1 mV/s or below. Study of the electro-oxidation of AHA using the EQCM in this time domain in acid solution (HNO₃ at pH 1) is complicated by two factors:

1. Mineral acid assisted dissolution of the Au surface;

2. The further promotion of that anodic dissolution by AHA, our desired overall objective.

EQCM study of the first effect indicates that the anodic dissolution reaction of gold in pH 1 HNO₃ is a 3 e⁻ process. The extent of the dissolution is sweep rate dependent due to (i) the longer dissolution times available at slower sweep rates; and (ii) the irreversibility of the soluble Au(III) electrogeneration process – the associated wave is displaced into the oxide generation peak at higher sweep rates. Indeed, at $v > 40$ mV/s, the classic cyclic voltammetric and voltamassogram behaviour of an insoluble, inert gold electrode in acid media is observed.

A detailed study of the anodic dissolution process of Au in HNO₃ solution containing various concentrations of AHA has been conducted as a function of pH using spectrophotometry and the EQCM. **Fig. 2** shows typical cyclic voltammograms and voltamassograms recorded in pH 1 HNO₃ at a sweep rate of 40 mV/s. In situ EQCM results demonstrate the following: (i) AHA does not absorb at the bare Au electrode surface at pH 1; (ii) Under acid conditions, and in agreement with the results of Amberson and Svehla [2], the electro-oxidation of AHA occurs by both 1 and 2 electron processes. The former gives rise to formation of a dimer, whilst the latter results in the production of ethanoic acid and a range of nitroso compounds. Both processes are diffusion controlled. (iii) At $v > 40$ mV/s, Au electrodisolution occurs almost entirely by an AHA-assisted one electron oxidation mechanism, mediated by the formation of a Au-AHA complex. Spectroscopic measurements, in conjunction with Pourbaix Diagram data, indicate that the resultant complex then auto-oxidises in free solution, producing AHA oxidation products and colloidal Au. (iv) At $E > \sim 1.3$ V vs. SCE, at pH 1, both the AHA oxidation and Au dissolution reactions cease due to electrode passivation.

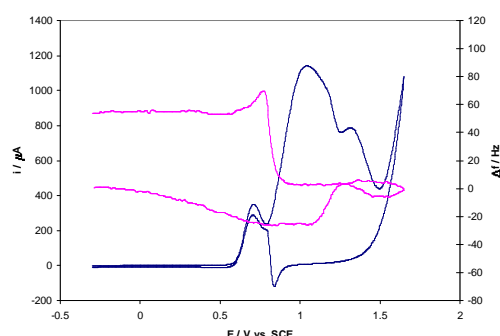


Figure 2: Cyclic voltammogram of 20mM AHA using a Au EQCM crystal at 40 mV/s.

Finally, EQCM data allows for the ready deconvolution of the AHA peaks from the CV (and voltamassogram) of the Au-nitric-AHA system shown in **Fig.2**, so facilitating the study of the 1 and 2 electron oxidation processes of AHA by polarography using a range of gold microelectrodes at pH 1 nitric acid. The results have been interpreted using the theoretical treatment of Oldham *et al* [3], and E^0 values for the oxidation of AHA obtained.

[1] A. Hamlin, *J. Electroanal. Chem.*, **407** (1996) 1; A. Hamlin, *ibid*, **407** (1996) 12, and references therein.

[2] J.A.Amberson and G.Svehla, *Anal.Proc.*, **23** (1986) 443

[3] K.B.Oldham, J.C.Myland, C.G.Zoski and A.M.Bond, *J.Electroanal.Chem.*, **270** (1989) 79.